Quantum Monte Carlo Study of Weakly Interacting Systems

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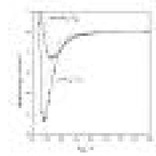
Fixed node diffusion Monte Carlo (DMC) and variational Monte Carlo (VMC) energies are calculated for two systems, water dimer and nitric oxide dimer, as examples of two different weak interaction energies. Using single determinant trial wave functions, comparison with experiments results with other levels of theory show good agreement in the preliminary results. This results important since QMC can be applicable to systems containing a large number of atoms and still get good values of this very small energies. The main result observed are result of the fixed node approximation and also the small number of blocks calculated at this time.

Introduction

Weak interactions dominate most biochemical interactions. Small energy differences have been difficult to determine accurately for large systems with available quantum chemical methods. In this project we investigated the applicability of quantum Monte Carlo to the determination of interaction energies of small, but very important systems. Two types of weak interactions were studied, hydrogen-bonding, represented by the water molecule and Van der Waals interactions, which were studied in the Nitric Oxide dimmer. Calculations were made using the QMC method and different tests were made using different trial wave functions, obtained at different levels of theory and different basis set quality.

NO dimer



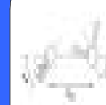
Simple oxides of nitrogen are interesting species for many reasons. They belong to the relatively few simple molecules which are usually viewed as stable compounds, but which possess an unpaired electron, and are strictly speaking free radicals.

Among the consequences of their open shell nature are their complex spectra with relatively low lying excited electronic states, Another consequence of the unpaired electron is the inclination of nitrogen oxides to form dimers, The structures of the neutral $(NO)_2$ dimer, and of its cation and anion, have been extensively studied, both experimentally and by theoretical means, but in spite of that the situation remains quite confusing. The actual conformations of these weakly bound species are still controversial, their structures poorly known and understood.

Most experimental evidence suggests a planar ***C_{2v} cis*** geometry for the neutral gas phase dimer, with a binding energy of merely about 1.8-2.3kcal/mol. Experimental information about the trans-NO-dimer is very scarse, possibly due to its much lower stability.

The dimer also proves to be a considerable challenge for theoretical ***ab initio*** calculations, and its electronic structure is still not well understood.

Water dimer



Water has always been an important subject of study in chemistry, either as a molecule by itself or as a solvent. Water molecules interact with each other via hydrogen bonding. In the quest to accurately describe the solid and liquid phases of water, people have tried to develop good intermolecular potential surfaces. One-way of doing this is to properly separate the pair wise, three-body, four-body, et. Interactions. The water dimmer interaction has been a subject of a large number of theoretical studies, becoming a benchmark system for interactions of polar molecules. Despite the effort, it is difficult to tell with accuracy of 1kcal/mol or better what the theoretical predicted value of this interaction energy is at the minimum of the potential. The values obtained for this interaction ranges from –4.1 to –6.1 kcal/mol. This spread is larger than the commonly accepted experimental range of –5.4±0.2 kcal/mol suggested in some experiments.

For the water dimer structure, Odutola and Dyke measured microwave spectra of $(H_2O)_2$, $(D_2O)_2$, and several mixed isotopes. Fitting these data to a model system, where the water monomers are fixed at the equilibrium structure of HOH = 104.52° and R_{OH} = 0.9572Å, they estimate that R_{OO} = 2.976 (+0.00, -0.03)Å; having a ***C_s*** point group symmetry.

Quantum Monte Carlo (QMC)

Shrödiger Equation

$$i\frac{\partial|\psi\rangle}{\partial t} = \hat{H}|\psi\rangle$$

VMC

$$\frac{\langle \Psi_T|\hat{H}|\Psi_T\rangle}{\langle \Psi_T|\Psi_T\rangle} = \frac{\int \Psi^* \hat{H} \Psi}{\int \Psi^* \Psi} \geq E_0$$

Where ***Eo*** is the energy for the ground state

DMC

Letting τ=***it***

$$\frac{\partial|\psi\rangle}{\partial \tau} = -\hat{H}|\psi\rangle$$

And solving this we get

$$|\psi(\tau_2)\rangle = e^{-\hat{H}(\tau_2-\tau_1)}|\psi(\tau_1)\rangle$$

Quantum Monte Carlo (QMC) methods are a powerful numerical approach to the investigation of Quantum Many-Body Systems. One of the main focus of our group is to develop the methodology and apply it to interesting many-body systems. There are different QMC techniques:

- Variational Monte Carlo (VMC) is used to evaluate quantum mechanical expectation values for a given trial wavefunction.
- Diffusion Monte Carlo (DMC) is based in the fact that the Schroedinger equation written in imaginary time will converge to the ground state exponentially fast. (This is also known as projector Monte Carlo or Green's Function Monte Carlo.)
- The Path Integral Monte Carlo method is a powerful computational tool to calculate thermodynamic properties of quantum many-particle systems at finite temperature.

In this work, only the VMC and DMC approaches are used. A VMC calculation is run using the wavefunction obtained form the calculations made using several levels of theory such as Hartree Fock (HF) or Density Functional Theory (DFT). After a first VMC calculation is run, correlation parameters are introduced and a new VMC calculation is made. A DMC calculation is made at the end using the output obtained from the last VMC run.

Preliminary Results

The next tables shows some results obtained for the water and NO dimmers, respectively, in previous works using different levels of theory and QMC

Method		H_2O-H_2O(kcal/mol)
QCISD	aug-cc-pVQZ	-4.83 (-4.66)
DFT/BLYP	aug-cc-pVQZ	-4.19 (-4.15)
DFT/B3LYP	aug-cc-pVQZ	-4.57 (-4.54)
DFT/BPW91	aug-cc-pVQZ	-3.58 (-3.54)
DFT/SVWN5 (LDA)	aug-cc-pVQZ	-8.76 (-8.70)
Plane wave DFT/LDA	24x24x24 cell 100 Rydberg cutoff	-8.88
Plane wave DFT/BLYP	20x20x20 cell 70 Rydberg cutoff	-4.33
Plane wave DFT/PBE	20x20x20 cell 70 Rydberg cutoff	-5.29
Quantum Monte Carlo		-6.4±0.4
Experiment		-5.4±0.7

Method	Energy(kcal/mol)	***cis***NO-NO(kcal/mol)
CASPT2(18,14) /6-311+G(2D)	-259.406569	4.31
CASPT2(18,14)/ cc-pVTZ	-259.463724	4.34
CASPT2(18,14)/ aug-cc-pVTZ	-359.507708	6.31
MRCI(10)+Q/6-311G(2d)	-259.329024	3.66
MRCI(6)+Q/6-311G(2d)	-259.321843	2.34
DFT-B3LYP/6-311G+(d)	-2.5985843	-3.00
CCSD(T)/aug-cc-pVDZ	--------	3.3
DFT-PLAP1 XC/6-311G+(d)	--------	8.18
Quantum Monte Carlo		-3.4±0.4
Experiment		2.0±0.3

Conclusions

- The results presented in this poster are only preliminary ones, more work needs to be done in order using QMC to get better results.
- The QMC results are in fairly agreement with those obtained using other levels of theory.
- It can be seen that in general, those methods that include the electronic correlation to the wavefunction in some way, give better results for this interaction energies.
- Also more diffuse basis sets help describe better the interaction region, giving rise to better energies.

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